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**THE EFFECTS OF CONCENTRATION ON POLARIZATION
CAPACITY AND POLARIZATION RESISTANCE IN
FERROCYANIDE - FERRICYANIDE CELLS
WITH PLATINUM ELECTRODES**

Technical Report No. 1

to the

OFFICE OF NAVAL RESEARCH

April 15, 1953

Research Contract

Nonr-604(00)

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By

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INTRODUCTION

It has long been known that an electrolytic cell through which an alternating current is passing exhibits both resistive and reactive characteristics. The history of research done on these characteristics has recently been reviewed by Shaw and Remick (1) and therefore need not be repeated here. It will suffice for our present purpose to review only those details which constitute the necessary background for an understanding of this report.

The resistive characteristics of an alternating current cell are two in number:

(1) The "true" electrolytic resistance, R_T , of the electrolyte between the electrodes and (2) the polarization resistance, R_Δ . These two components of the total equivalent series resistance, R_s , of the cell are related to it by the equation;

$$R_s = R_T + R_\Delta \quad (1)$$

or

$$R_s = \frac{l}{a\kappa} + R_\Delta \quad (2)$$

where l is the interelectrode distance in centimeters, κ is the specific conductance of the electrolyte and a is the electrode area in square centimeters which must be the same as the cross sectional area of the conducting path. Eq. (2) has been rigorously established by Jones and Christian (2).

The reactive characteristic of an alternating current cell is usually expressed as an equivalent series capacitance, C_s , and is called the polarization capacitance. It is considered to be made up of two components; the electrical double layer capacity, C_d , and a pseudo-capacity, C_p . It is probably not correct, however, to write $C_s = C_d + C_p$ since Grahame (3) has shown that the equivalent circuit for half of an electrolytic cell is almost certainly that given in fig. (1) where θ is a pure resistance, W is a non-linear circuit element called the Warburg impedance, i_c is the charging current, i_f the faradaic current and i_t the total current. The potential drop from A to B may be symbolized by e_{AB} ; it is the drop across the double layer, the electrode surface being at A. The pseudo-capacity is related to the Warburg impedance as described below.

The faradaic branch of the circuit is the one of chief interest to chemists who are studying the mechanisms of reactions occurring at electrodes: Grahame (3) has recently developed a mathematical theory of the faradaic admittance according to which the resistance θ seems to be the modern equivalent of the old and practically discarded concept of "chemical resistance". More precisely, it represents the partial derivative of e_{AB} with respect to i_r , the relationship being regulated by the activation energy of the electron transfer reaction occurring at the electrode. The Warburg impedance owes its existence to another slow process, diffusion, which affects the potential because diffusion regulates the concentrations of electro-reducible and electro-oxidisable substances at the electrode surface and these concentrations regulate the potential according to the Nernst equation. Quantitatively, Grahame defines the Warburg impedance as $1/C_s^* \omega^{1/2}$ when θ is zero. Here C_s^* is the equivalent series capacitance of the faradaic branch of the circuit of fig. (1) and ω is the frequency of the alternating current in radians per second.

The term pseudo-capacity has been used loosely to designate that part of the cell capacity which arises from any causes other than the charging of the double layer. It may now conveniently be defined quantitatively in terms of Grahame's theory as being identical with C_s^* .

The polarization resistance R_p finds no place as such in Grahame's theory. He prefers to use the equivalent series resistance R_s^* of the faradaic branch of the circuit and shows that

$$R_s^* = \theta + \eta / \omega^{1/2}$$

where η is a complicated function of diffusion coefficients, transference numbers and partial differential coefficients related to the Nernst equation. Thus we see that R_s^* can be broken up into two components, one related to the activation energy of the discharge process, the other to diffusion and transference. For the purposes of the present report, R_s^* may be considered identical with the "pseudo-resistance", R_p .

A mathematical theory, similar in many regards to Grahame's, has rather recently been published by Ershler (20).

The original objective of the work described in the present report was to study the properties of polarization resistance and pseudo-capacity, to develop a supporting theory and to apply this knowledge to a study of oxidation-reduction mechanism. Grahame's report on the mathematical theory of the faradaic admittance did not become available to us until many months after our research was well under way. Its advent suggested expanding our original aims to include checking our data against his theory, as far as that is possible at the present time.

Of the many variables which affect the values of polarization capacitance and polarization resistance we will deal in this report only with the electrolytic concentration. A brief history of previous research on this subject will be given in the following paragraphs.

All investigators agree that C_g increases with the concentration. Typical of the electrodes and electrolytes which have been employed are the following: silver nitrate with silver electrodes (2), strong mineral acids with platinum or mercury electrodes (5), neutral inorganic salts with platinum, silver, nickel or mercury electrodes (4, 6), mixtures of ferrocyanide and ferricyanide with platinum electrodes (1). The results of these investigations may be interpreted to mean that C_g increases with the concentration of electrolyte regardless of whether or not a faradaic process is operative.

The effect of concentration on the double layer capacity has been formulated in terms of the thermodynamic theory of electrocapillarity (7) but this phase of the problem is by no means a closed book.

A special phase of the concentration problem, which arises when both components of a reversible redox system are present in solution, is the effect of "redox ratio" on C_g and its components. (The term "redox ratio" is used by us to mean specifically the ratio of the concentration of the oxidant to that of its conjugate reductant). Work on this problem was started by Shaw and Remick (1) who showed that the polarization capacitances of ferrocyanide-ferricyanide mixtures approach a maximum as the redox ratio approaches unity.

It appears that R_d increases as the electrolytic concentration decreases. Typical of the systems investigated are the following: platinum electrodes in sodium chloride solution (4), gold electrodes covered with finely divided gold in potassium chloride (8), silver electrodes in silver nitrate (2), mercury in dilute solutions of mercurous nitrate in 2N aqueous perchloric acid solution (19). An exception to this tentative generalization was found by Jones and Christian (2) who observed that R_d decreased with the concentration in the case of smooth platinum electrodes in potassium chloride solution.

Grahame (6), using mercury electrodes in various salt solutions, found that R_d is zero when no faradaic current flows.

In developing his mathematical theory of the faradaic admittance, Grahame (3) gave no consideration to the possibility that poorly conducting electrode layers might contribute to R_d . While this possibility might be justifiably ignored in dealing with scrupulously clean dropping mercury electrodes, such as he used in his own work, it should be given serious consideration when solid electrodes are used. Indeed there is definite evidence that such surface layers are formed. Scott (9) showed that such is the case when lead electrodes are used and Shipley (10), working with silver or copper electrodes at three cycles per second, visually observed the alternating appearance and disappearance of colored electrode coatings which he considered to be oxides. Shipley's rather well supported theory of the critical current density (10, 11) explains that phenomenon in terms of saturation of the electrodes with electrolytic gases. Considerable attention has also been given to passivation of electrodes by means of alternating currents (12, 13, 14). Passivation strongly suggests oxide coatings. Thus

there is ample evidence that electrode layers are formed during alternating current electrolysis, at any rate when high current densities are used. Although no one, as far as we are aware, has definitely shown that these electrode layers contribute to R_{p} , there is a large amount of well known evidence from direct current studies indicates that such might well be the case. There is also the possibility that platinum electrodes, for example, might not be freed from their oxide coatings by the electrode cleaning operation and that these coatings might make appreciable contributions to the values of R_{p} .

Apparently no experimental investigations have been published which deal with quantitative correlations of concentration with pseudo-capacity and polarization resistance or with an analysis of the concentration effect into terms of its dependent variables such as ionic strength, diffusion rates and electrical migration rates.

EXPERIMENTAL METHOD

Measurements of the resistance and capacitance of the electrolytic cell were made by means of an impedance bridge constructed in the same general manner and using the same circuit elements as the bridge described by Shaw and Remick (1) except that, (1) shielded wire was used much more judiciously than previously (to improve the freedom from frequency dependency), (2) both the source of alternating current and the oscillograph used as a null point detector were isolated from the bridge by shielded transformers (General Radio type 578-B), (3) a Ballentine model 300 electronic voltmeter was used as a voltage amplifier in the detector circuit, (4) the power amplifier was shielded, and (5) a somewhat different type of electrolytic cell was used. As before, the cell was immersed in a constant temperature bath kept at $30^{\circ} \pm 0.1^{\circ}$, purified nitrogen was bubbled through it and the platinum electrodes employed were made by sealing platinum discs in glass tubing so that the platinum surfaces were flush with the ends of the tubes. The new features of the cells were: (1) the electrodes were mounted one above the other and the upper electrode was mounted in a threaded brass sleeve so that the inter-electrode distance could be varied and measured with a cathetometer, and (2) a piece of glass tubing, open at both ends, was slipped over the electrodes. Its inside diameter was just large enough to allow the free motion of the upper electrode within it and its upper end projected above the surface of the solution. Its purpose was to provide a conducting path of fixed diameter so that the inter-electrode distance would be the only geometrical variable.

The "true" electrolytic resistance of the solution, R_{T} , and the polarization resistance, R_{p} , were determined by the method introduced by Miller (15) and used effectively by Jones and Christian (2). This method is based on Eq. (2) from which it is seen that a plot of R_{g} against the inter-electrode distance will give a straight line with an R_{g} intercept equal to R_{D} . Eq. (1) can then be used to calculate R_{T} for each inter-electrode distance.

The cleaning of the electrodes will be discussed in the following section of this report.

The potassium sulfate, potassium ferrocyanide and potassium ferricyanide used were Baker's analysed reagents. The sodium benzenesulfonate was prepared from a "practical" grade of benzene sulfonic acid and twice recrystallized.

REPRODUCIBILITY OF ELECTRODES AND HYSTERESIS

The difficulty of getting reproducible measurements with metallic electrodes under non-equilibrium conditions is well known. Nevertheless platinum electrodes were chosen for our investigations in preference to dropping mercury electrodes because we wished to develop a technique that could be used in studying the mechanisms of oxidation of organic compounds which require anodic potentials exceeding the dissolution potential of mercury. Furthermore, uniform current density cannot be attained and resistance measurements encounter grave difficulties when dropping electrodes are used in the frequency range in which we are most interested (19).

The cathodic cleaning of electrodes in alkaline cyanide, used by Shaw and Remick (1), was found not to give sufficiently good reproducibility so that the results of independent runs made, for example, at different concentrations could be compared with each other. Months of effort were expended in seeking a satisfactory method of cleaning platinum electrodes. We tried hot aqua regia, hot nitric acid, anodic cleaning and cathodic cleaning in alkaline cyanide or in nitric acid, mechanical polishing and finally silver and gold plating. We tried various combinations of these treatments and various lengths of time.

The method finally adopted was the following one. An electrode made from new platinum was immersed in the alkaline cyanide solution recommended by Shaw and Remick (1) and cleaned anodically for two minutes and cathodically for four minutes using 3 volts with an electrode separation of about 1.8 cm. This cycle was performed three times. The electrode was then washed very quickly with distilled water, then with a portion of the cell solution and immersed in the cell. Electrodes so prepared gave steady readings after about 30 minutes immersion and never changed after that by more than 2% on standing for 24 hours.

A related difficulty occurs when electrodes are subjected to high current densities. When the current density gets high enough a sort of "hysteresis" sets in. Bridge readings become unstable, drifting with time, and if the current density is lowered the resistance and capacitance show reluctance to return all the way to their former values. A similar "hysteresis" was observed by Slygin and Frumkin (16) in making direct-current charging curves for platinum in aqueous sulfuric acid.

Since we were interested in making semi-quantitative studies at high current densities, it was obviously desirable to eliminate or correct for hysteresis if that were possible. With this goal in mind we attempted to establish its cause. We do not feel that our studies of hysteresis merit any detailed description but a brief comment on them seems to be in order. We consider that the most likely cause of hysteresis is the collection of electrolytic gases on the electrode. This could easily account for the accompanying instability of bridge readings and would only make its appearance above a certain current density value. This theory is also supported by our observation that hysteresis sets in at a much lower current density when ferrocyanide alone is present in solution than when a poised ferrocyanide-ferricyanide solution is used. In the former case, ferrocyanide is oxidized during the anodic half cycle and hydrogen ions are reduced during the cathodic half cycle (17). When the poised solution is used, the cathodic half-cycle will reduce ferricyanide instead of hydrogen ions at moderate current densities.

We also observed that hysteresis increases when the current continues to flow at a constant rate. This observation suggests that, owing to the sluggish reversibility of the redox reactions producing hydrogen or oxygen, the layer of gas continually builds up on the electrode.

The formation of a layer of adsorbed gas would be expected to increase the resistance. Such an increase was observed.

The dissolution of platinum is a conceivable cause of hysteresis, but in none of our experiments was hysteresis accompanied by a visible change of the electrode surface. Furthermore, in the experiment with the ferrocyanide solution, one would not expect dissolution of platinum at the moderate current densities used. The latter remark would apply equally to the possibility that hysteresis is caused by the formation of an unstable oxide whose instability would account for the observed instability of the bridge readings. It is not impossible that unstable compounds are produced electrolytically from ferro- or ferricyanides, but this explanation could hardly apply to the hysteresis observed with potassium sulfate solution, although in this case a higher current density was required to produce the hysteresis.

Strictly speaking, it is not a critical value of the current density which causes the onset of hysteresis but rather a critical value of the half-wave area (i.e., the number of coulombs per half cycle) or the peak voltage (which would increase with the half-wave area). This we demonstrated with a solution containing 0.005 mole per liter each of ferrocyanide and ferricyanide. At a frequency of 1000 c.p.s. and a current density of 111 ma cm⁻² there was no hysteresis, but very strong hysteresis was encountered at 55 ma cm⁻² at 200 c.p.s. These observations are in accord with our tentative theory of hysteresis.

It is apparent that if our suggested explanation of hysteresis is correct, we are not likely to find a way of avoiding it at high current densities using platinum electrodes in aqueous solutions.

RESULTS OF EARLIER IMPEDANCE BRIDGE MEASUREMENTS

Before we had discovered a method of preparing reproducible electrodes we made a large number of experiments which gave excellent precision within a single "run", as judged by the smooth curves obtained, but which could not be quantitatively reproduced if the electrodes were recleaned between runs. Nevertheless, the curves obtained on duplicate runs always showed the same general characteristics so we feel they are qualitatively reliable. Insofar as these earlier experiments dealt with relationships not reinvestigated later with our refined technique, they will be presented briefly in this section of our report.

The Effect of Current Density on Capacitance and Resistance.

It is well known that if capacity measurements are made with solutions such as aqueous sulfuric acid or sodium chloride that increasing current densities are not accompanied by any appreciable change in capacity until the current density reaches a value called "the capacitive elevation point" (C.E.P.). Beyond this point the capacity rises rapidly with the current density. Shaw and Remick (1) presented evidence to support the theory that the C.E.P. is the point at which the activation energy hump associated with the electrolytic decomposition of water is overcome. They remarked that this phenomenon should not occur when reversible systems are used. Nevertheless they observed a C.E.P. with an equimolar solution of ferrous and ferric sulfates using frequencies ranging from 1000 to 10000 c.p.s.

Whether or not this unexpected result is related to their unfortunate choice of frequencies or, as they suggested, to an unfortunate choice of current densities, we do not know. We can report, however, that we observed no C.E.P. with poised ferrocyanide-ferricyanide solutions. Instead, a "capacitive depression point" (C.D.P.) was found. This is illustrated by fig. 2. A typical resistance plot is shown in fig. 3. Although the ionic strength was 0.382 in the solution used for fig. 2 and 0.530 for fig. 3 (in other regards the solutions were alike; 0.005M in both oxidant and reductant, supporting electrolyte K_2SO_4 , frequency 200 c.p.s., interelectrode distance 1.83 cm), similar curves were obtained in all runs. In all cases a "resistive elevation point" (R.E.P.) occurred at the same current density as the C.D.P. The maximum in the R_s curve is real, as shown by other experiments in which readings were taken at higher current densities. It was also observed that the R.E.P. increases with the frequency. Finally, it is of interest to note that in still other experiments with the ferricyanide-ferrocyanide system in which it was attempted to make check runs we found that although the absolute values of C_s and R_s did not check (due to our inability up to that time to find an effective method of cleaning our electrodes), the values of the C.D.P., the R.E.P. and the maximum in the R_s curve checked very well.

The theoretical explanation of the C.D.P. is quite obvious. Since in these solutions the values of C_s ranged from 250 to 500 microfarads per square centimeter, it is apparent that C_s is largely a pseudocapacity

which is very probably the result of the reversible electrochemical polarization one would expect with a reversible redox system (18). Accordingly, when the alternating current excursions (and therefore the voltage excursions) are small, the limits of the poised region of the Nernst electrode potential curve are not exceeded and the differential capacity (dQ/dE) is essentially constant. It is also very large in the poised region. When the voltage excursions are increased sufficiently, the limits of the poised region are exceeded and the capacity should fall. That it actually does so is additional evidence in favor of this theory of pseudocapacity. The observation, that C.E.P.'s are associated with irreversible electrode reactions while the existence of a C.D.P. indicates a reversible electrode reaction in a poised solution, could conceivably serve a diagnostic purpose in studies of reaction mechanism.

The theory of the R.E.P. is not equally clear. We will not pursue it further at this time.

The Relationship between Cell Voltage and Current.

We have consistently observed in our experiments with ferrocyanide-ferricyanide mixtures that a plot of current density against cell voltage (measured with an electronic voltmeter) is linear up to rather high current densities. This is illustrated by fig. 4. This can only mean that the impedance is constant in this range despite the fact that the values of C_s and R_s are far from constant (cf. fig's. 2 and 3). This constant impedance explains why no distortion of either our current or voltage waves was ever detected oscillographically in this range of current densities. If it were otherwise, we would not be justified in making calculations of equivalent series capacitance and resistance from impedance bridge measurements.

The observation of such a linear relation for a circuit containing a non-linear circuit element (viz., the Warburg impedance) suggests that we have discovered in this relation an important clue to the nature of the Warburg impedance, at least where poised reversible redox systems are involved. Before jumping to this conclusion, however, we must consider the possibility that the large pseudocapacity results in a capacitive reactance so small that it is negligible in comparison to the resistance, that therefore the equivalent series impedance is essentially equal to R_s and that the relatively small deviation of R_s from constancy (cf. fig 3) results in an essentially linear relation between E and I . To answer this criticism, consider that the deviation in E caused by the deviation ΔR in R_s is

$$\Delta E = \left(\frac{\partial E}{\partial R} \right) \Delta R$$

Introducing Ohms law and values of I and R taken from fig. 3, this equation becomes

$$E - I \cdot R = 0.040 \text{ amp} \times 2.7 \text{ ohms} = 0.108 \text{ volt}$$

This is ten times any observed deviation of E in the linear range of fig. 4.

Apparently, then, the linearity in question represents a fundamental property of the ferrocyanide-ferricyanide cell and possibly of all reversible oxidation-reduction cells. We are not prepared to pursue the theoretical interpretation of this observation further at this time.

RESULTS OF LATER IMPEDANCE BRIDGE MEASUREMENTS

The measurements described in this section of our report were made with platinum electrodes cleaned by the improved method which already has been described. These measurements, in contrast to those described in the preceding section of this report, were all made at low current densities (1.52 ma cm^{-2}).

In order to establish the reproducibility of electrodes prepared by this method, the electrodes were immersed in a solution of $0.005M$ ferrocyanide and $0.005M$ ferricyanide containing enough potassium sulfate to give a total ionic strength of $0.231M$, allowed to stand 20 - 40 minutes and bridge measurements made at a frequency of 800 c.p.s. The electrodes were then removed and cleaned again. This complete cycle was carried out nine times. The mean deviation was $1.5 \mu F \text{ cm}^{-2}$ (0.78%) for C_s and 0.2 ohm (0.31%) for R_s . The corresponding maximum deviations from the mean were $4 \mu F \text{ cm}^{-2}$ (2.1%) and 0.5 ohm (0.77%). As a further check on reproducibility, a completely independent check run was made on the dispersion of C_s and R_s at ionic strength $0.231M$ (table 1). The resistance measurements checked to within a few tenths of an ohm and the capacitance measurements within $2 \mu F \text{ cm}^{-2}$ except at 400 c.p.s. where the deviation was 4.4 and at 200 c.p.s. where it was 18 (or 5.2%).

Tables 1 to 4 give the data collected in our study of the effects of ionic strength, supporting electrolyte and concentration of depolarizer on C_s , R_s and R_L and their dispersions. All measurements were made at $30^\circ \pm 0.1^\circ$.

The Effect of a Supporting Electrolyte.

If alternating current techniques are to be used as reliable and versatile tools in studying oxidation-reduction mechanism, it is essential that we first understand the influence of concentration in general and of supporting electrolytes and ionic strength on the directly measured variables. For example, if it is desired to study the oxidation or reduction of organic compounds it will usually be necessary to add a supporting electrolyte to render the solution sufficiently conducting. It

thus becomes necessary to know what effects to expect from the supporting electrolyte and to correct for them quantitatively, if need be. Or again, it might be desirable to study the effect of altering the redox ratio and since this cannot be done without altering the concentration of one of the redox components it would again be necessary to know how to make corrections for the effect of the concentration change as such. As another example of the practical necessity for this knowledge might be mentioned the probability that variations in the concentration of the supporting electrolyte or of the ionic strength as such could well be made to yield information on the charge type of the participating species in a redox reaction. Finally, studies of the type under discussion can contribute valuable data for qualitative and quantitative tests of existing theories.

Table I shows the variation of C_s , R_s and R_d with the ionic strength at constant concentration of depolarizer. Table IV shows the corresponding measurements at constant total ionic strength and variable concentration of depolarizer. From these data the following conclusions can be drawn.

- (1) C_s increases with the ionic strength slightly and with the depolarizer concentration markedly. (Cf., fig. V).
- (2) R_d decreases markedly as the ionic strength increases. Its variation with depolarizer concentration is slight; at frequencies of 600 c.p.s. and higher it increases with the concentration while at lower frequencies the results are uncertain, but they seem to indicate that in the presence of sufficient excess of supporting electrolyte R_d is essentially independent of depolarizer concentration.

In order to determine whether the so-called effect of ionic strength (Table I) is really that rather than something else, sodium benzene-sulfonate was used in place of potassium sulfate as supporting electrolyte at a total ionic strength of 0.23M (Table III). Comparison of these two tables shows that the results are not sufficiently accurate to enable us to state with certainty that C_s will have the same values in solutions of these two supporting electrolytes at the same ionic strength, other things being equal, but at least the data are not incompatible with this conclusion. The data do show, however, that R_d is accurately the same in each case. This conclusion taken together with conclusion # 2 above shows that the effect of concentration on R_d is largely if not entirely an ionic strength effect in poised aqueous solutions of ferrocyanide and ferricyanide in the presence of a supporting electrolyte.

Fig. 6 gives a plot of the capacitance data from Table IV. It shows clearly that in the presence of sufficient supporting electrolyte C_s is a linear function of the depolarizer concentration and that the rate of change of C_s with the concentration is greater at lower frequencies, the half-wave area being constant.

The points corresponding to the highest concentration do not fall on the straight lines. This we ascribe to the absence of supporting electrolyte in this solution. Since the ionic strength was the same in all four solutions, we can conclude that at least a part of the effect of the supporting electrolyte on C_d is something other than an ionic strength effect. It is presumably the elimination of the electrical migration of the ferrocyanide and ferricyanide ions.

Dispersion studies.

In studying the dispersion of R_s and C_s it is necessary to decide whether the voltage, current or half-wave area (i.e., the number of coulombs per half-wave of current) is to be kept constant. Corresponding respectively to these three conditions we may study "E-dispersion", "I-dispersion" or "Q-dispersion". Which of these types of dispersion will be chosen depends on the purpose for which the measurements are made.

If it is desired to obtain C_d by extrapolation of a plot of C_s against the reciprocal of the square root of the frequency, one should pick conditions so that C_d is constant. C_d is a function of E_{AB} (cf., Fig. I) but is independent of frequency as such (6). Ideally, then, the dispersion should be measured at constant E_{AB} . Strictly speaking, this would demand an alternating current of infinitesimal amplitude. The best we can do is to use a very low current density and recognize that an increasing frequency can then influence our cell in two fundamentally different ways:

(1) The half-wave area is decreased (at constant current) and (2) The Warburg impedance is increased. The decreased half-wave area reduces the number of coulombs passing through the cell (at constant I) so that E_{AB} is decreased and C_d changes. To some extent this decrease of E_{AB} is counterbalanced by the increase in the Warburg impedance and the decrease in double layer impedance accompanying the increase in frequency. These influences both operate to alter the coulombic partition between the faradaic and non-faradaic branches in favor of the latter so that E_{AB} will increase somewhat as a result. This second factor should be of relatively small importance, however, so that we may conclude that Q-dispersion is to be preferred to I-dispersion since the first influence is thereby eliminated entirely. In regard to E-dispersion, it must be remembered that it is impractical to keep E_{AB} constant. If the cell voltage is kept constant, the alteration of cell impedance due to both of the influences under discussion will result in an alteration of IR_T so that constant cell voltage does not mean constant E_{AB} . In view of these considerations, we chose to measure Q-dispersion in our later studies. The results of our dispersion studies will be discussed in the two succeeding sections of this report.

Electrode Layer Resistance.

In our "earlier impedance bridge measurements" we found that I-dispersion plots of R_s against the reciprocal of the square root of the frequency were usually linear and that always the extrapolated value of R_s at infinite frequency was higher than R_T as determined by extrapolation to zero interelectrode-distance. Inasmuch as the latter method gave the

same values of R_T as determined by the Kohlrausch method (i.e., using platinized electrodes), it was deemed reliable and the higher values obtained by the frequency extrapolation interpreted to mean that there must be at the electrode surface a frequency-independent component of R_s . In terms of Grahame's theory, the impedance of the faradaic branch of the circuit is infinite when the frequency is infinite so this component of R_s cannot be in the faradaic branch. If it is true, as Grahame thinks is true for clean surfaces, that the resistance in the non-faradaic branch of the circuit is zero, then this component of R_s must fit into Fig. 1 to the left of A, in series with R_s . It is hard to imagine what it would be except the resistance of a poorly conducting layer on the electrode surface, so we will tentatively call it the "electrode-layer resistance" and symbolize it as R_1 . This means that Eq. (1) now must be rewritten as

$$R_s = R_T + R_1 + R_\Delta \quad (4)$$

when platinum electrodes are involved, R_Δ remaining the only frequency-dependent component.

The pertinent data are given in Table V. The electrodes were "cleaned" by a variety of methods resulting in a wide variety of values for R_1 . It is interesting to note that the lowest value of R_1 was obtained in the only run in which the electrodes were polished. (Subsequent to polishing they were cleaned cathodically in alkaline cyanide.) These results are compatible with the conclusion that at least a part of R_1 is caused by a surface layer left on the electrode by the cleaning process (or produced by it).

Table V also indicates a parallelism between R_1 and C_s which shows that the values of C_s are very sensitive to those of R_1 .

The dispersion measurements made after we discovered a satisfactory means of getting reproducible electrode surfaces were all of the Q-dispersion type. The experimental values are given in Tables I-IV and the calculated values of R_1 in Table VI. The plots of R_s against the reciprocal of the square root of the frequency were all strictly linear except the one marked with a double asterisk. The following conclusions can be drawn from these data.

- (1) R_1 is always positive.
- (2) R_1 is not a function of the electrode cleaning process alone because it increases as the depolarizer concentration increases and decreases as the concentration of the supporting electrolyte increases, other things being equal.
- (3) Our improved method of cleaning electrodes makes a constant contribution to the value of R_1 as shown by the last two lines of Table VI.
- (4) Plots of the reciprocal of R_Δ , as defined by Eq. (4), against the molar concentration of depolarizer at constant ionic strength, are linear. The slopes are positive and increase with the frequency.

Determination of the Double Layer Capacity

It will be explained later that if we are to use our data for a precise quantitative test of the validity of Grahame's theory for measurements made with platinum electrodes, we must first measure the double layer capacity. Ordinarily this is done by extrapolating a plot of C_s against the reciprocal of the square root of the frequency to infinite frequency. Such plots made from our data are linear but the uncertainty in the extrapolated values amounts to as much as 2 microfarads/cm². Since C_d itself is of this same order of magnitude in our solutions, this degree of precision is not sufficiently good for the proposed test of the theory.

It is common practice in polarography to determine the charging current from measurements on the supporting electrolyte alone. Although we felt grave doubts about the general validity of this method, it suggested that measurements of the capacity made on the supporting electrolyte alone might yield a reasonably accurate value of C_d . The data are given in Table II. The capacitance values there given show a Q-dispersion, which suggests that in addition to the true double layer capacity an additional source of capacitance is present. This same conclusion is also in accord with the fact that these values are considerably higher than those determined from the data on poised solutions by extrapolation of C_s to infinite frequency. A plot of the C_s values from Table II against the reciprocal of the square root of frequency is far from linear.

We are working on an oscillographic method of determining C_d . The method, although inadequately tested, seems to give consistent results of relatively high precision, but we have not convinced ourselves that what we are measuring is really the double layer capacity. Rather than postpone this report any longer, we have decided to let this phase of our work as well as the related application of our data to a precise quantitative test of Grahame's theory await our next technical report.

Theoretical Interpretations

All of Grahame's theoretical equations (3) are developed for the faradaic branch of Fig. I. This means that from our values of C_s and R_s , which are related to the whole cell, we must calculate C_s^* and R_s^* which are the equivalent series capacitance and resistance for the faradaic branch of half of the cell. The conventional method of alternating current circuit analysis suffices to relate these pairs of values. If we let \bar{Y} represent the vector admittance we may write

$$\bar{Y}_F = \bar{Y}_{AB} - \bar{Y}_d \quad (5)$$

where the subscripts have meanings obvious from Fig. I. We also wish to consider a series combination of R_s^* and C_s^* whose vector admittance, \bar{Y}^* , is equal to \bar{Y}_F . Equating the two and using Eq. (5) we get:

$$\bar{Y}_{AB} - \bar{Y}_d = \bar{Y}^*$$

or, expressing each admittance in the conventional way, we may write:

$$2 \frac{(R_s - R_T)}{(R_s - R_T)^2 + X_s^2} + j \left(\frac{2X_s}{(R_s - R_T)^2 + X_s^2} - \frac{1}{X_d} \right) = \frac{R_s^* + jX_s^*}{(R_s^*)^2 + (X_s^*)^2}$$

where X_s , X_s^* and X_d are the reactances corresponding to C_s , C_s^* and C_d respectively and j is the imaginary operator. If we now equate the horizontal and vertical components separately, we get the two equations:

$$2 \frac{R_s - R_T}{(R_s - R_T)^2 + X_s^2} = \frac{R_s^*}{(R_s^*)^2 + (X_s^*)^2} \quad (6)$$

$$\frac{2X_s}{(R_s - R_T)^2 + X_s^2} - \frac{1}{X_d} = \frac{X_s^*}{(R_s^*)^2 + (X_s^*)^2} \quad (7)$$

These two equations may now be solved simultaneously to get:

$$R_s^* = \frac{M}{M^2 + N^2} \quad (8)$$

and

$$C_s^* = \left(\frac{M^2 + N^2}{N} \right) \frac{1}{\omega} \quad (9)$$

where

$$M = \frac{2(R_s - R_T)}{(R_s - R_T)^2 + X_s^2} \quad (10)$$

and

$$N = \frac{2X_s}{(R_s - R_T)^2 + X_s^2} - \frac{1}{X_d} \quad (11)$$

It is obvious from the above equations that R_s^* and C_s^* cannot be calculated without knowing the value of the double layer capacity. Since, as was explained in the preceding section, we have not yet been able to get sufficiently accurate values of the double layer capacity, this very important comparison of our data with Grahame's theory must await the solution of this difficulty.

There is possible, however, one semiquantitative check of our data with Grahame's theory which can be made without knowing the double layer capacity. The following mathematical development is necessary for this purpose.

Eq. 37 of Grahame's report (3) is:

$$\eta = \sum_i \beta_i v_i / \sqrt{2\epsilon_i} \quad (12)$$

where

$$\beta_i \equiv \partial E / \partial w_i \quad (13)$$

Here w_i is the concentration of the substance W_i at a distance from the electrode "just exceeding that at which the effect of the double layer begins to be appreciable." It may be taken as the concentration in the bulk of the solution. When the diffusion occurs in the aqueous phase and a supporting electrolyte is present in a sufficiently high concentration to reduce the transference numbers of the depolarizer ions to zero, ν_i is the number of equivalents of an ion produced by chemical action when one faraday of electricity crosses the phase interface. According to Grahame's conventions ν_i has a value of -1 for ferricyanide ions and +1 for ferrocyanide ions. Finally D_i is the diffusion coefficient of the substance W_i .

If we express the Nernst equation in terms of concentrations rather than activities and use the American conventions with regard to sign, we get:

$$E = E_0 - (RT/nF) \ln (w_{ox}/w_{red})$$

where w_{ox} and w_{red} are the bulk concentrations of ferricyanide and ferrocyanide respectively. Differentiation of this equation with respect to concentration and combination with Eq. (13) gives us the two equations:

$$\beta_{ox} = \partial E / \partial w_{ox} = -RT/nF w_{ox} \quad (14)$$

$$\beta_{red} = \partial E / \partial w_{red} = RT/nF w_{red} \quad (15)$$

Combination of Eq's. (12), (14) and (15), introduction of the numerical values for ν and recognition that in our poised solutions $w_{ox} = w_{red} = w$, yields the equation:

$$\eta = \frac{RT}{nFw} \left(\frac{\sqrt{2\epsilon_{red}} + \sqrt{2\epsilon_{ox}}}{2 \sqrt{\epsilon_{ox} \epsilon_{red}}} \right) \quad (16)$$

Grahame's Eq. (39) may be written in terms of our symbols as:

$$C^*_s = 1/\eta \omega^{1/2} \quad (17)$$

Combination of Eq's. (16) and (17) gives:

$$C^*_s = \frac{2nFw}{RT\sqrt{\omega}} \left(\frac{\sqrt{\epsilon_{ox} \epsilon_{red}}}{\sqrt{2\epsilon_{red}} + \sqrt{2\epsilon_{ox}}} \right) \quad (18)$$

If the temperature and frequency are held constant and if we assume, as a first approximation, that in the presence of an appreciable excess of supporting electrolyte and at constant ionic strength the diffusion coefficients are independent of the concentration of the depolarizer, Eq. (18) becomes:

$$C^*_S = k^*w \quad (19)$$

Similarly Eq. (16) can be substituted into Eq. (3) to give the equation:

$$R^*_S = \theta + \frac{k^*}{w} \quad (20)$$

Since we are dealing with a reversible redox system, θ should be essentially zero, so that Eq. (20) becomes

$$R^*_S = k^*/w \quad (21)$$

Substitution of Eq's. (19) and (21) together with the definition of X^*_S into Eq. (6) gives:

$$\frac{1}{w} \cdot \frac{2(R_S - R_T)}{(R_S - R_T)^2 + X^*_S} = k'' \quad (22)$$

The validity of this equation can readily be tested since all quantities on the left hand side of the equation are known from experiment. Introduction of the data from Table IV into this equation gave values of k which showed no indication of constancy at a given frequency.

One need not seek far for an explanation of this failure if one remembers that our experiments indicated that an additional resistance, R_1 , must be added to Fig. 1 to give an equivalent circuit which adequately represents our cell. If we assume that R_1 is in series with the rest of the circuit, it follows that the quantity $R_S - R_T$ in Eq. (22) should be replaced by $R_S - R_T - R_1$. This quantity we may call R_Δ and Eq. (22) becomes:

$$\frac{1}{w} \cdot \frac{2R_\Delta}{R_\Delta^2 + X^*_S} = k \quad (23)$$

Values of k calculated from the data in Table IV are given in Table VII. In the last column are listed the percent deviations of k from the mean. In view of the assumptions which went into Eq. (22) and the high relative experimental errors in the small R_Δ values, especially above 1000 c.p.s., the constancy of k is gratifying. The conclusion seems justified that, to a first approximation at least, Grahame's theory adequately represents the effect of variations in the concentration of the depolarizer in the presence of a large excess of supporting electrolyte and at constant ionic strength when platinum electrodes are used in poised ferrocyanide-ferricyanide solutions -- provided that a correction is made for the presence of an "electrode layer resistance".

Until we succeed in measuring C_d more accurately, the only possible further comparisons of our data with existing theory are qualitative in nature.

Our observation that changes in the ionic strength exert only a small influence on C_s is to be expected since ionic strength, according to

Grahame's theory, affects C_s^* only through its effect on η which in turn is affected only because the redox ratio in the Nernst equation was expressed in terms of concentration rather than activity and because diffusion constants are slightly dependent on inter-ionic attraction. By the same token and in view of the similarities of Eq's. (3) and (17) and the similar relations of R_s^* and C_s^* in the equivalent circuit, one might expect likewise that R_D would not be much affected by the ionic strength. We have seen, however, that the opposite is true. We plan to give more consideration to this question in the near future.

The dependence of C_s and R_D on w , experimentally observed in the presence of an excess of supporting electrolyte, can be represented by the equations:

$$C_s = k_1 w \quad (24)$$

$$R_D = k_2 / w \quad (25)$$

Similar relations hold for Grahame's C_s^* and R_s^* as shown by Eq's. (19) and (21). To ascertain whether or not our experimental observations are qualitatively consistent with Grahame's theory, Eq's. (24), (25), (19) and (21) may be introduced into Eq. (7), whereupon we get the equation

$$1/X_D = k_3 w \quad (26)$$

This equation demonstrates consistency with theory only in case it is true that the double layer capacity increases with w at constant frequency in the presence of an excess of supporting electrolyte. This would be true if the ferrocyanide and ferricyanide ions were preferentially adsorbed on platinum (6). We do not know whether or not this is true.

TABLE I

Q-DISPERSION AS A FUNCTION OF IONIC STRENGTH

Ferrocyanide (0.005M)
 Ferricyanide (0.005M)
 Supporting Electrolyte: K_2SO_4
 Half wave area = 0.685 microcoul./cm²
 Inter-electrode distance = 1.80 cm
 Electrode Area = 0.253 cm²

Capacitance given in microfarads/cm², resistance in ohms

Ionic Strength	0.2314			0.3821			0.5300			0.6805		
Freq.	C _s	R _s	R _L	C _s	R _s	R _L	C _s	R _s	R _L	C _s	R _s	R _L
200 c.p.s.	343.5	207.0	75.0	359.2	127.8	49.7	369.9	96.1	37.1	397.6	78.0	31.3
400	252.1	204.0	72.0	258.1	125.1	47.0	267.5	93.2	34.2	278.1	75.8	29.1
600	200.9	202.8	70.8	202.5	124.6	46.5	215.2	92.0	33.0	215.1	74.9	28.2
800	174.8	202.2	70.2	176.3	124.0	45.9	185.3	91.4	32.4	192.2	74.3	27.6
1000	156.1	201.7	69.3	153.8	123.7	45.6	168.6	90.9	31.9	173.7	73.8	27.1
1500	122.8	201.0	69.0	127.1	122.9	44.8	134.6	90.2	31.2	138.8	73.0	26.3
2000	100.3	200.6	68.6	103.6	122.4	44.3	112.5	89.7	30.7	118.2	72.6	25.9
2500	86.9	200.5	68.5	88.6	122.2	44.1	97.7	89.5	30.5	101.4	72.5	25.8
3000	77.1	200.1	68.1	88.0	121.9	43.8	90.5	89.4	30.4	92.6	72.3	25.6
3500	69.9	199.9	67.9	73.4	121.7	43.6	82.8	89.0	30.0	84.9	72.1	25.4
4000	63.5	199.8	67.8	67.6	121.5	43.4	77.9	88.8	29.8	78.6	71.9	25.2
5000	53.4	199.4	67.4	57.9	121.1	43.0	67.8	88.7	29.7	69.9	71.7	25.0
	R _T = 132.0			R _T = 78.1			R _T = 59.0			R _T = 46.7		

TABLE II

Q-DISPERSION OF C_s FOR SUPPORTING ELECTROLYTE

Potassium sulfate
 Half wave area = 0.685 microcoul./cm²
 Inter-electrode distance = 1.80 cm
 Electrode area = 0.253 cm²
 Capacitance given in microfarads/cm²

Ionic strength Freq.	0.231M C_s	0.3821 C_s	0.5300 C_s	0.6805 C_s
200	8.94	9.12	9.11	9.10
400	8.78	8.82	8.88	8.93
600	8.63	8.66	8.82	8.85
800	8.48	8.55	8.73	8.78
1000	8.37	8.44	8.67	8.74
1500	8.08	8.23	8.53	8.64
2000	7.88	8.08	8.41	8.56
2500	7.70	7.93	8.31	8.45
3000	7.53	7.82	8.18	8.36
3500	7.32	7.71	8.10	8.29
4000	7.17	7.60	8.01	8.21
5000	6.96	7.34	7.84	8.08

TABLE III

Q-DISPERSION IN SODIUM BENZENESULFONATE SOLUTION

Ferrocyanide = 0.005M

Ferricyanide = 0.005M

Supporting electrolyte = sodium benzene sulfonate

Ionic Strength = 0.231M

Half wave area = 0.685 microcoulombs/cm²

Interelectrode distance = 1.80 cm

Electrode Area = 0.253 cm²R_T = 142.0 ohms

Freq.	C _s	R _s	R
200	350.7	216.9	74.9
400	249.6	214.1	72.1
600	203.3	212.6	70.6
800	172.5	212.2	70.2
1000	156.9	211.9	69.9
1500	125.2	211.2	69.2
2000	105.9	210.9	68.9
2500	91.2	210.6	68.6
3000	83.2	210.4	68.4
3500	75.2	210.2	68.2
4000	67.8	210.0	68.0
5000	60.5	209.7	67.7

TABLE IV

Q-DISPERSION AS A FUNCTION OF CONCENTRATION OF DEPOLARIZER

Depolarizer: ferrocyanide + ferricyanide
 Redox ratio = unity
 Supporting electrolyte = K_2SO_4
 Half-wave area = 0.685 microcoulombs/cm²
 Inter-electrode distance = 1.80 cm
 Electrode area = 0.253 cm²
 Ionic strength = 0.6805

M(Ox. Red.)	0.005M			0.010M			0.015M			0.0425M*		
Freq.	C _S	R _S	R _D	C _S	R _S	R _D	C _S	R _S	R _D	C _S	R _S	R _D
200	397.6	78.0	31.3	736.9	78.7	30.7	1096	81.0	30.3	2693	101.1	34.1
400	278.1	75.8	29.1	534.1	77.1	28.9	763.7	80.0	29.3	1998	100.9	33.9
600	215.1	74.9	28.2	430.7	76.9	28.4	638.4	79.7	29.0	1611	100.8	33.8
800	192.2	74.3	27.6	380.5	76.6	28.1	569.1	79.5	28.8	1466	100.7	33.7
1000	173.7	73.8	27.2	342.3	76.4	27.9	517.0	79.3	28.6	1311	100.6	33.6
1500	138.8	73.0	26.3	282.9	76.0	27.5	427.2	79.1	28.4	1137	100.5	33.5
2000	118.2	72.6	25.9	237.7	75.8	27.3	351.4	78.9	28.2	1069	100.4	33.4
2500	101.4	72.5	25.8	210.3	75.7	27.2	312.7	78.8	28.1	932	100.4	33.4
3000	92.6	72.3	25.6	194.5	75.6	27.1	294.3	78.8	28.1	785	100.3	33.3
3500	84.9	72.1	25.4	175.3	75.5	27.0	265.5	78.7	28.0	699	100.3	33.3
4000	78.6	71.9	25.2	162.7	75.4	26.9	245.8	78.6	27.9	681	100.2	33.2
5000	69.9	71.7	25.0	145.0	75.2	26.7	226.9	78.5	27.8	646	100.1	33.1
	R _T = 46.7			R _T = 48.5			R _T = 50.7			R _T = 67.0		

*Ferrocyanide and ferricyanide only (no supporting electrolyte)

TABLE V

RELATION OF C_s AND ELECTRODE LAYER RESISTANCE

Concentration of ferrocyanide 0.005M
Concentration of ferricyanide 0.005M
Supporting electrolyte K_2SO_4
Ionic strength 0.3821
Interelectrode distance 1.81 cm
Frequency 200 c.p.s.
Capacitance given in microfarads per cm^2

R_s	R_T	R_1	C_s
107.5	77.9	23.8	498
105.7	78.5	20.0	468
104.9	77.6	16.8	428
116.0	78.9	9.0	336

TABLE VI

VALUES OF R_1 FROM Q-DISPERSION DATA

The experimental values are in Tables I and IV except for the "check run"

Ionic Strength	Molarity of oxidant and reductant	R_1
0.6805	0.0125*	33.0
0.6805	0.0150	27.4
0.6805	0.0100	25.9
0.6805	0.0050	23.7
0.5300	0.0050	27.8
0.3821	0.0050	40.9**
0.2314	0.0050	65.8
Check run 0.2314	0.0050	64.8

* No supporting electrolyte

** Plot of R_g against $1/\sqrt{\omega}$ was slightly curved

TABLE VII*

VALUES OF k CALCULATED BY EQ. (23)

Freq.	R_{Δ}	X_S	w	k	dev.
200	7.6	2.001	0.005	49.2	8.3%
200	4.3	1.080	.010	43.7	3.7
200	2.9	0.726	.015	43.3	4.6
400	5.4	1.431	.005	69.2	5.2
400	3.0	.745	.010	62.8	4.6
400	1.9	.521	.015	65.3	0.8
600	4.5	1.233	.005	82.7	5.1
600	2.5	.616	.010	75.4	4.2
600	1.6	.415	.015	78.1	0.8
800	3.9	1.036	.005	95.8	5.9
800	2.2	.523	.010	86.1	4.9
800	1.4	.349	.015	89.7	0.9
1000	3.4	1.145	.005	105.7	6.2
1000	2.0	.581	.010	92.2	7.4
1000	1.2	.385	.015	100.6	1.1
1500	2.6	.764	.005	141.1	10.0
1500	1.6	.375	.010	118.5	7.8
1500	1.0	.248	.015	125.7	2.2
2000	2.2	.673	.005	166.4	7.6
2000	1.4	.335	.010	142.8	7.6
2000	0.8	.226	.015	154.6	0.0
2500	2.1	.628	.005	175.0	5.6
2500	1.3	.303	.010	146.1	11.8
2500	0.7	.203	.015	176.1	6.3
3000	1.9	.573	.005	192.9	8.9
3000	1.2	.273	.010	158.9	10.3
3000	0.7	.180	.015	179.5	1.4
3500	1.7	.536	.005	213.8	8.6
3500	1.1	.259	.010	171.9	12.7
3500	0.6	.172	.015	205.1	4.2
4000	1.5	.506	.005	240.0	8.0
4000	1.0	.245	.010	188.7	15.1
4000	0.5	.162	.015	238.1	7.1
5000	1.3	.455	.005	273.7	2.4
5000	0.8	.219	.010	231.9	13.2
5000	0.4	.140	.015	296.3	10.8

* Note that the R_{Δ} of this table differs from that of tables I-IV in that it includes a correction for R_1 .

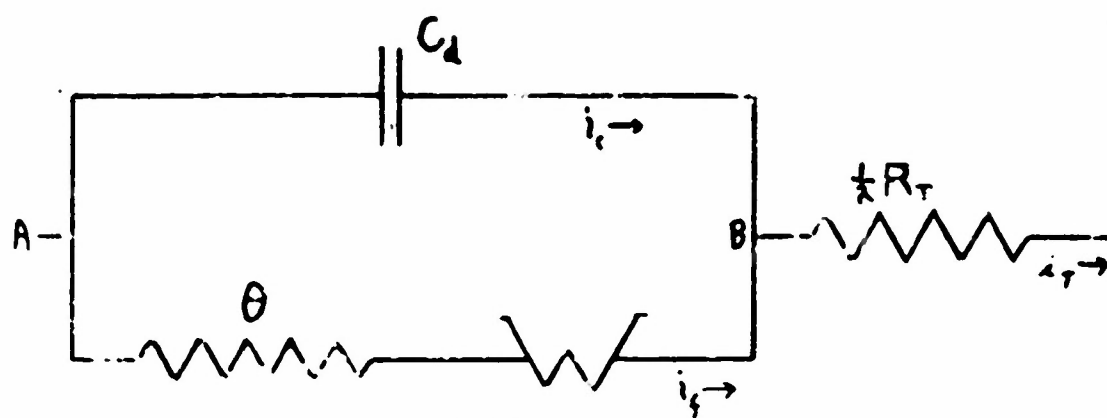


FIG. I

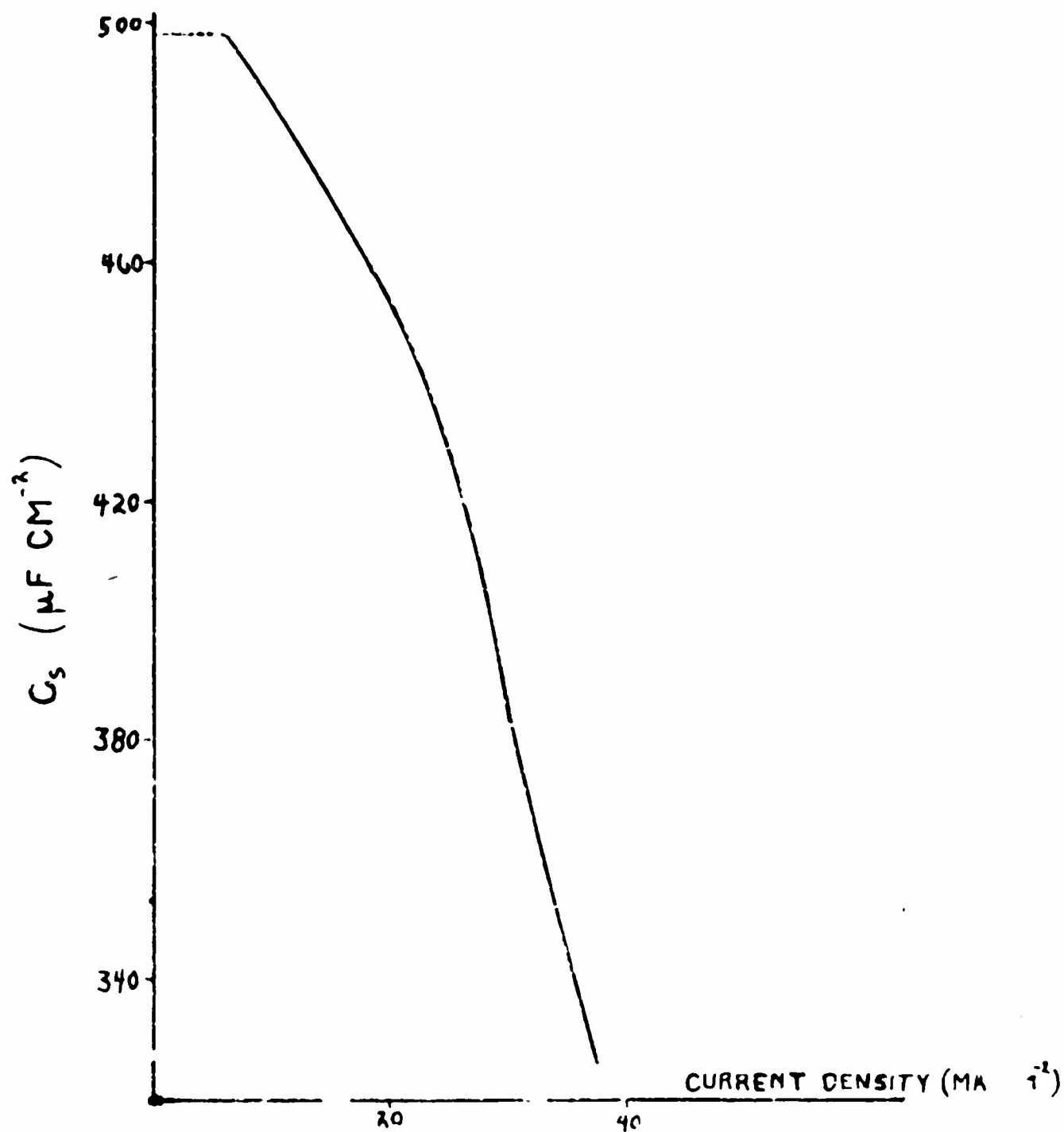


FIG. II

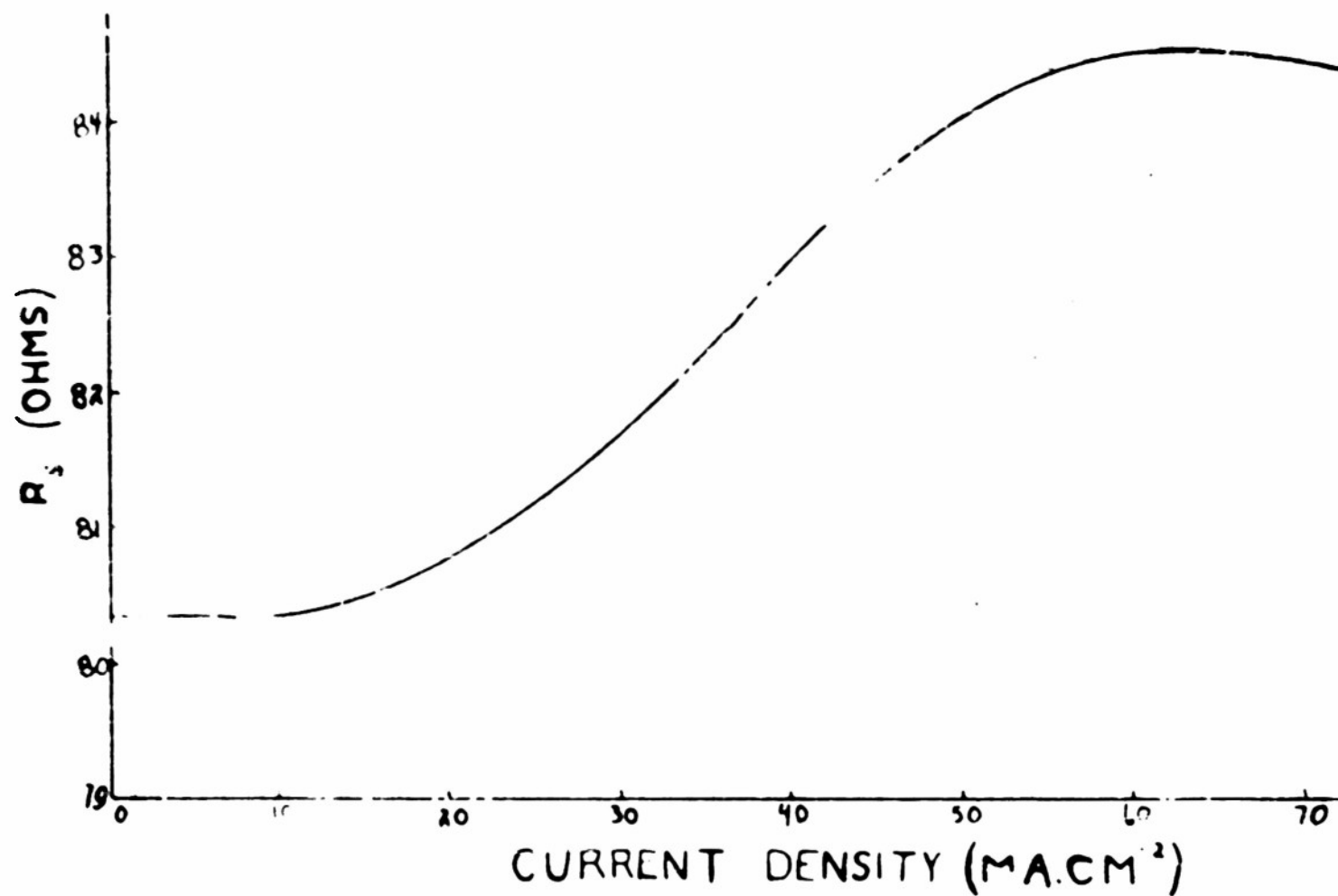


FIG. III

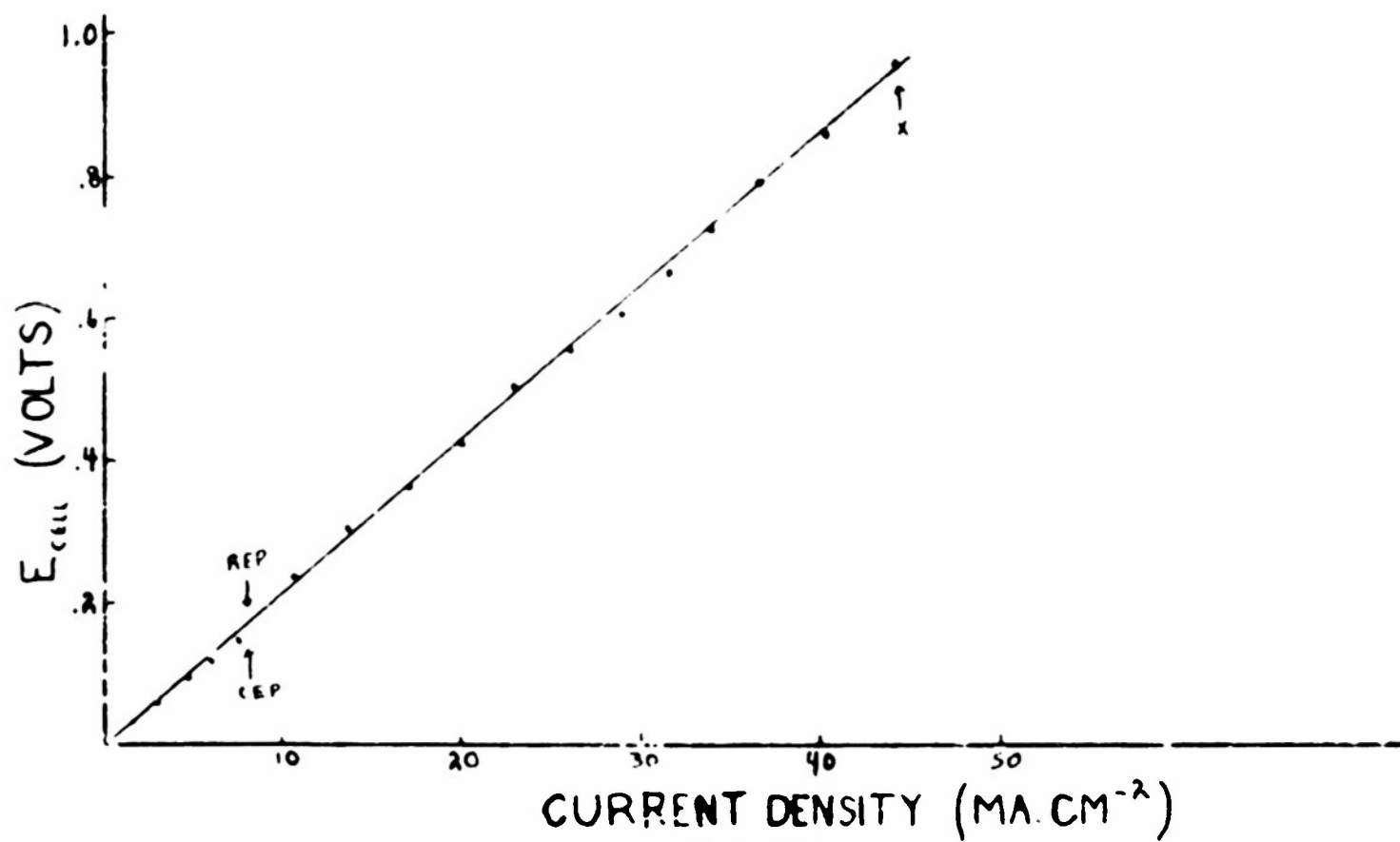


FIG. IV

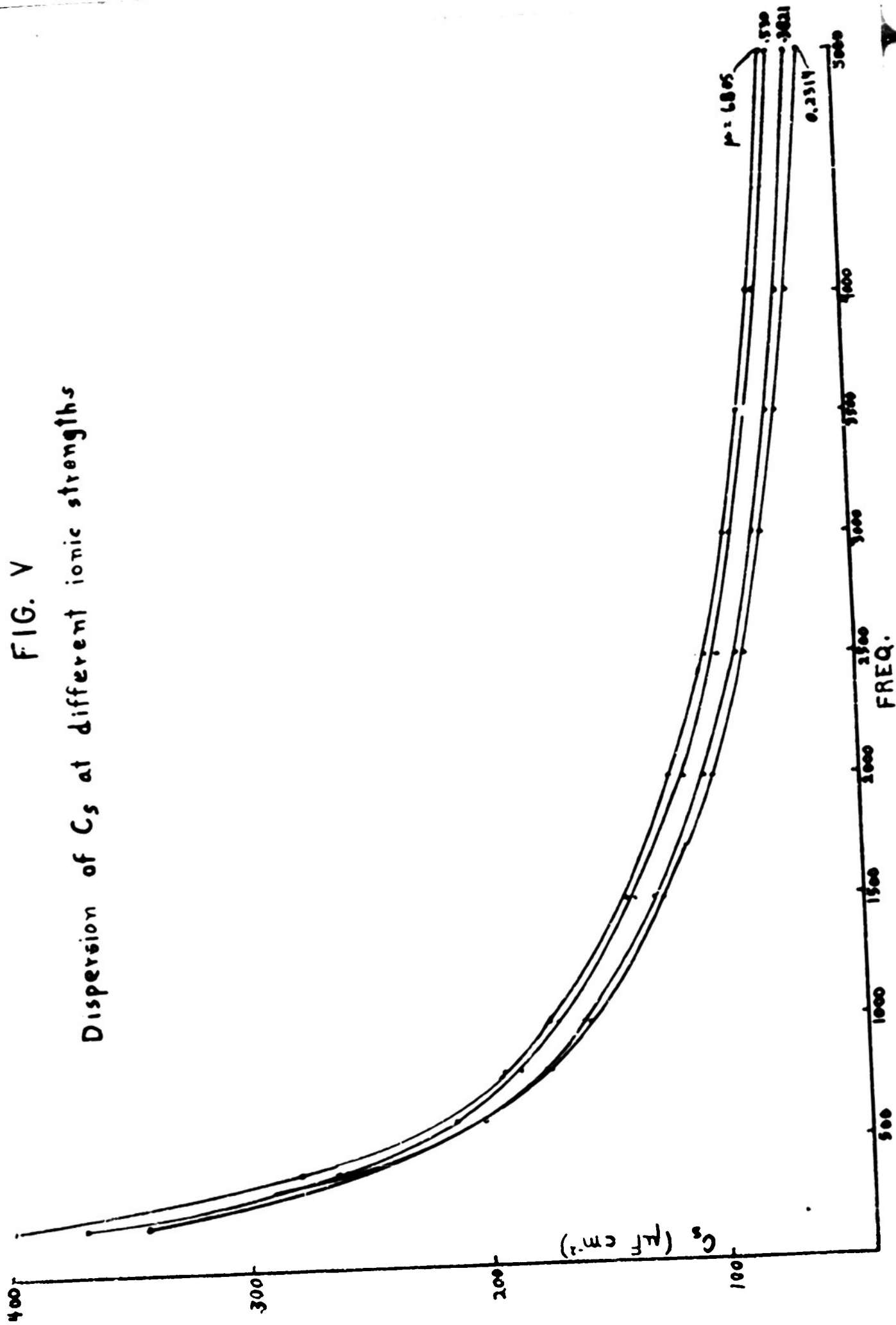
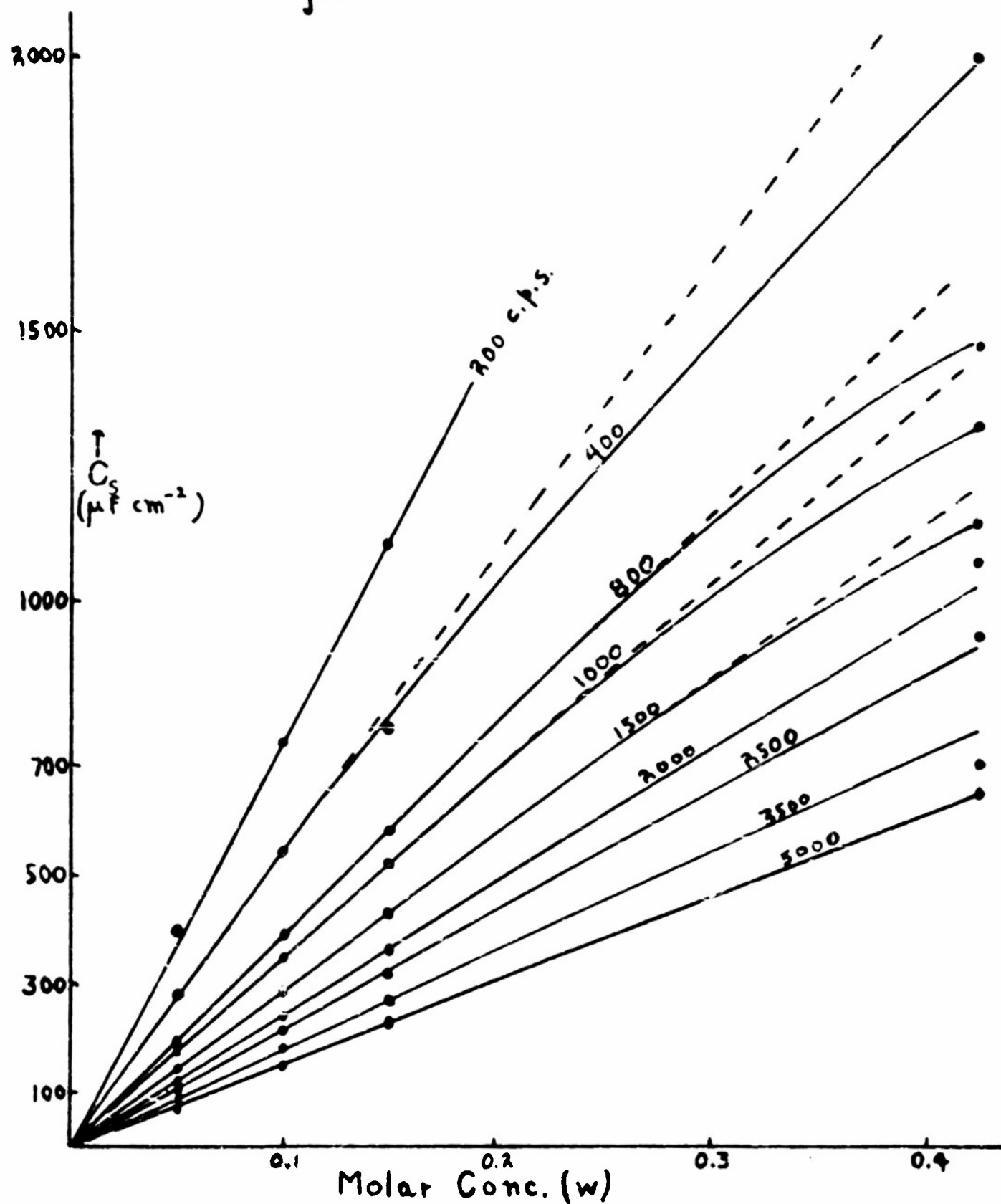


FIG. VI
 C_s -CONCENTRATION CURVES AT
VARIOUS FREQUENCIES

Ionic Strength 0.6805



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